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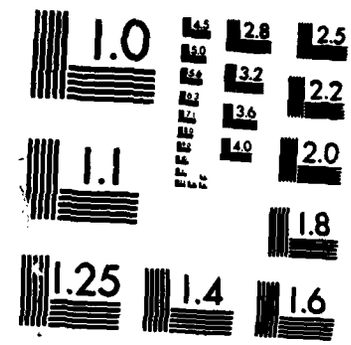

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Nonlinear Optical Processes in Organic and Polymeric Crystals and Films

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Physical studies have demonstrated that organic and polymer structures possess unusually large, ultrafast second and third order nonlinear optical properties in a large number of material structures, phases, and states that include organic crystals, monomolecular films, polymer structures, liquid crystals and liquid crystal polymers. For two such polymer systems, PBI and PBT, third harmonic generation measurements show that they possess large non-resonant third order optical susceptibilities whose origin resides in ultrafast,

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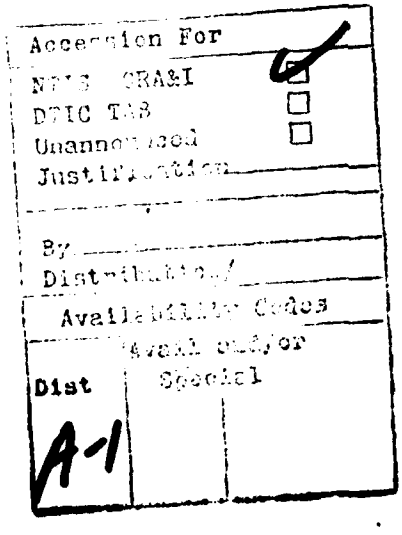
lossless excitations of highly charge correlated pi-electron states.

Multilayer thin films have been fabricated as organic superlattices by the Langmuir-Blodgett technique to produce finite sequences of from one to several hundred molecular monolayers of different amphiphilic molecules. When one of the molecules contains a pi-electron system the macroscopic nonlinear optical properties of such thin films can be controlled. FINAL REPORT, AFOSR-84-0135, Nonlinear Optical Processes in Organic and Polymeric Crystals and Films.



Summary

Physical studies have demonstrated that organic and polymer structures possess unusually large, ultrafast second and third order nonlinear optical properties in a large number of material structures, phases, and states that include organic crystals, monomolecular films, polymer structures, liquid crystals and liquid crystal polymers. Theoretical calculations have shown that the basic origin of these properties resides in highly charge correlated excited states of the π-electron distribution comprising these structures. These striking properties together with demonstrations of phase conjugate wave generation, optical bistability, and associative memory networks have stimulated considerable growth in research and development activities in centers throughout the world. A wide variety of potential applications in advanced optical technologies are being actively pursued that include optical signal processing and computing, image reconstruction, data storage and telecommuications.

The intrinsic response time for electron excitations is ultrafast (10^{-14} - 10^{-15} sec). In general, a nonlinear optical polarization in a medium involves either resonant absorptive, or non-resonant reactive, nonlinear responses. A reactive nonlinear response is due to lossless virtual optical excitations in the nonlinear medium with no net population changes or any material transformations which do occur in an absorptive response. Examples include non-resonant harmonic generation, frequency

mixing, and optical Kerr effects. By far the fastest response times occur in reactive nonlinear media since reactive responses do not involve relatively slow material changes of the nonlinear medium. Moreover, among the possible virtual excitations of reactive responses, electron excitations of order 10^{-15} seconds (1 fs) are intrinsically faster than phonon excitations which involve much slower nuclear displacements and vibrations of order 10^{-12} seconds (1 ps).

For large classes of conjugated molecules and polymer structures, the remarkable property is that the nonlinear optical responses are dominated by lossless virtual excitations of the π-electron states, especially those possessing large charge correlations. This property was first demonstrated in second order responses. For example, in crystalline solids only electronic excitations contribute to second harmonic generation, whereas both electron and phonon excitations contribute to the linear electrooptic effect. For MNA (2-methyl-4-nitroaniline) crystals, for example, the large second harmonic susceptibility $\chi_{111}^{(2)}(-2\omega;\omega,\omega)$ of 500 x 10^{-12} m/v was shown to be the same as the linear electrooptic susceptibility $\chi_{111}^{(2)}(-\omega;\omega,0)$ = 540 x 10^{-12} m/v within experimental error demonstrating that the second order response is primarily purely electronic with little or no lattice contribution, and thus intrinsically fast. Examples at the molecular level include the magnitude, sign, and frequency

dependence of the microscopic second order response of organic molecular structures such as MNA and the parent PNA. In third order processes for the case of a liquid crystal polymer, values of the non-resonant, electronic third order optical susceptibility for divinyldiacetylene (DVDA) liquid crystal monomers and polymers were found to be two orders of magnitude greater than that of reference glass and quartz.

High performance nonlinear optical polymer structures

As discussed earlier, rapid advances in the field will be achieved only through further development of stable, high performance polymer structures because optical media must ultimately possess important secondary properties that include mechanical, thermal, chemical, and oxidative stabilities in addition to optical quality fabrication and high through-put processing into desired shapes and conformations. Furthermore, polymer structures can be designed for their linear and nonlinear optical properties at the microscopic scale by suitable selection of pendant side groups and monomer repeat units. Macroscopic symmetry can be controlled, for example, by incorporating chiral centers for noncentrosymmetry, or by applying external mechanical stress, electric, or magnetic fields, especially in liquid crystal phases. For two such polymer systems, PBI and PBT, third harmonic generation measurements show that they possess large non- resonant third order optical susceptibilities whose origin

resides in ultrafast, lossless excitations of highly charge correlated π-electron states.

X-ray Structure of Langmuir-Blodgett Multilayer Thin Films

Multilayer thin films can be fabricated as organic superlattices by the Langmuir-Blodgett technique to produce finite sequences of from one to several hundred molecular monolayers of different amphiphilic molecules. Both periodic and quasi-periodic sequences can be constructed using two, or more, molecules of different incommensurate chain lengths. If one of the molecules contains a π-electron system possessing a large nonlinear optical response, the macroscopic nonlinear optical properties of such thin films can be controlled. This depends critically on the nature of the structural ordering of the molecular sites along the profile axis of the multilayer perpendicular to the layer planes as well as in the plane of the monolayers. Most methods of unambiguous structural analysis employing x-ray scattering require the repetition of some average structural unit (unit cell) in a periodic array of effectively infinite extent. We have employed novel methods in the analysis of the x-ray scattering perpendicular to the layer planes from finite periodic multilayer films containing from two to ten molecular monolayers and from quasi-periodic multilayer structures. The latter have been utilized to prove that the

surface monolayer at the multilayer-air interface is disordered in such thin films and that ordering of the surface monolayer occurs on subsequent deposition of an additional bilayer.

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